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(54) A PROCESS FOR THE PRODUCTION OF MODIFIED POLYBUTADIENE

(71) We, BAYER AKTIENGESSELLSCHAFT, a body corporate organised under the laws of the Federal Republic of Germany of 509 Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of modified polybutadiene.

It is known that mercaptans can undergo addition reactions with butadiene polymers. It is also known that these addition reactions take place much more quickly with 1,2-double bonds than with 1,4-double bonds of the polybutadiene.

Since considerable difficulties arise in these reactions, for example in the distribution of molecular weight, as a result of uncontrollable crosslinking reactions or extensive degradation and olfactory irritation attributable to incomplete conversion, mercaptan-modified polymers of this type have not yet been adopted for use on a commercial scale.

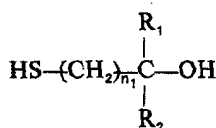
On the other hand, there is considerable commercial interest in polar-modified polybutadiene, for example for use in silica-containing rubber mixtures. Pure hydrocarbon elastomers, such as polybutadiene, polyisoprene or SBR, show very poor compatibility with highly active silicas and give vulcanisates with inadequate properties. Attempts have been made to solve these problems by using processing aids. Although the addition of, for example, mercaptosilanes as processing aids improves the compatibility of polybutadiene with silica, these very expensive compounds have to be used in quantities of 10% by weight and more, based on the rubber. As a result, these difficulties are not satisfactorily solved either from the economic or from the technical point of view.

The addition reaction of 2-mercaptoethanol with polybutadiene of narrow molecular weight distribution with a 1,2-double bond content of from 6 to 12% is described in German Offenlegungsschrift No. 1,816,394, whilst the addition of mercaptoamines is described in German Offenlegungsschrift No. 1,910,177. In both cases, the addition reaction is intended to take place preferentially with 1,4-double bonds of the polybutadiene. The reactions described in these two publications are incomplete so that working up on a technical scale is seriously complicated by the olfactory irritation caused by unreacted mercaptan. In addition, our own investigations have shown that the use of polybutadiene with a 1,2-double bond content of from 6 to 20% and the addition of mercaptans involve a very real danger of undesirable crosslinking. Under technical conditions, gel formation cannot be avoided. Products of this type show a very greatly reduced plasticity and cannot be processed by the methods normally used in rubber technology.

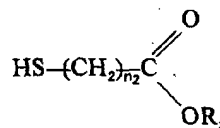
Polybutadiene with a high content, for example 80% and more, of 1,2-double bonds undergoes addition reactions with mercaptans, such as 2-mercaptoethanol and thioglycollic acid, very quickly and completely. Unfortunately, these addition products have a rather high glass transition temperature (T_g) and are therefore unsuitable for use as synthetic rubber.

An object of the present invention is to produce polar-modified uncross-linked polybutadiene with good processing properties and a sufficiently low glass transition temperature.

Accordingly, the present invention provides a process for the production of mercaptan-modified polybutadiene with a 1,2-double bond content of from 30 to 60%, preferably from 40 to 50%, and with viscosity numbers $[\eta]$ of from 0.8 to 1.8 dl/g (as measured in toluene at 25°C), wherein polybutadiene is reacted in solution with mercaptans corresponding to the general formulae (I) and (II):



(I)



(II)

in which

R_1 , R_2 and R_3 represent hydrogen or, being the same or different, represent a straight-chain or branched alkyl or aryl radical,

n_1 is a number from 1 to 4, and

n_2 is a number from 1 to 5.

The mercapto compounds corresponding to the general formulae (I) and (II) above are, generally, used in such quantities that the molar ratio of mercaptan to 1,2-double bonds in the polybutadiene amounts to between 0.1 and 0.6 and preferably to between 0.2 and 0.4.

If the 1,2-double bond content falls below 30%, there is a danger of cross-linking and an incomplete reaction could occur. If the double bond content rises far above 60%, products with rather high glass temperatures are obtained after modification.

Preferred mercaptans of formula (I) are compounds in which R_1 and R_2 represent hydrogen, C_{1-4} -alkyl or phenyl. Methyl and ethyl radicals are particularly preferred as alkyl radicals. 2-Mercaptoethanol, 2-mercaptoisopropanol, 1-phenyl-2-mercaptoethanol, 3-mercaptopropanol and 4-mercaptobutanol are mentioned by way of example.

Preferred mercaptans of formula (II) are compounds in which R_3 represents hydrogen or a C_{1-4} -alkyl radical, such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl or tert.-butyl. Thioglycolic acid and thioglycolic acid esters are mentioned as examples.

The production of butadiene polymer with a 1,2-double bond content is familiar to the expert and may be carried out, for example, by using *n*-butyl lithium and certain quantities of donors (e.g. glycol dimethyl ether or *N,N'*-tetramethyl ethylene diamine).

The reaction of the polybutadiene with the mercaptans of general formulae (I) and (II) is carried out in inert solvents, preferably hydrocarbons such as, for example, hexane, cyclohexane or toluene, the polymer concentration preferably amounting to between 10 and 30% by weight.

The reaction proceeds by a radical mechanism and is, therefore, initiated and controlled by radical-forming compounds such as, for example, alkyl hydroperoxides, dialkyl peroxides, diacyl peroxides or azo compounds. Azodiisobutyronitrile is preferably used as an initiator.

The reaction is, generally, carried out at 50°C to 150°C, according to the rate at which the initiator decomposes. In cases where azodiisobutyronitrile (AIBN) is used, the reaction is preferably carried out at temperatures in the range of from 60 to 90°C.

The reaction time required to obtain complete conversion of the mercaptan is normally between 2 and 10 hours, depending upon the reaction temperature applied. On completion of the reaction, a conventional stabiliser, such as for example 4-methyl-2,6-di-tert.-butyl phenol or 2,2'-dihydroxy-3,3'-di-tert.-butyl-5,5'-dimethyl diphenyl methane, is added to the polymer solution in quantities of from 0.1 to 1% by weight, based on the polymer.

The modified polybutadiene is isolated by precipitation with a non-solvent, for example methanol, ethanol or isopropanol. On a commercial scale, the solvent is preferably removed by steam distillation.

The polymer is dried in the usual way, for example in a drying cabinet or by means of a screw machine.

The polymers according to the invention may be processed in the machines normally used in the rubber industry, such as mixing rolls, internal mixers, and calenders, and are preferably used in silica-containing mixtures.

These mixtures are used, for example, for the production of treads for winter tyres and "off-the-road" tyres. In addition, the polar-modified butadiene polymers according to the invention are used in silica-containing steel cord compounds. In this case, there is no need for special adhesives to be added.

The following Examples illustrate the invention. The percentages are by weight.

EXAMPLE 1.

A solution of 4000 g of polybutadiene containing 42% of 1,2-double bonds and having a viscosity number $[\eta]$ of 0.9 (as measured in toluene at 25°C) in 22 kg of toluene was introduced into a stirrer-equipped vessel in the absence of air. 440 g of 2-mercaptoethanol were then added while stirring, followed by heating to 75°C. A solution of 8 g of azodiisobutyronitrile (AIBN) in 500 g of toluene was then introduced into this mixture. The mixture was then stirred for 5 hours at a reaction temperature of 75°C. After cooling to room temperature, a solution of 12 g of 2,2'-dihydroxy-3,3'-di-tert.-butyl-5,5'-dimethyldiphenyl methane in 100 g of toluene was added. The solvent was removed by steam distillation. The water-moist polymer crumbs were dried *in vacuo* at a temperature of up to 60°C. Dried polymer was obtained in a quantity of 4400 g, corresponding to a yield of 99%.

Sulphur, observed: 4.0%

Sulphur, calculated: 4.0%

The conversion amounts to 100%

The viscosity number $[\eta]$ was 0.97 dl/g in toluene at 25°C ML-4' 100°C = 50 (according to ASTM 927-5T)

Defo H/E = 850/33 (according to DIN 53 514)

Glass temperature $T_g = -42^\circ\text{C}$ (differential thermoanalysis).

EXAMPLE 2.

Various quantities of thioglycollic acid were reacted under the reaction conditions described in Example 1 with a polybutadiene having a viscosity number $[\eta]$ of 0.88 (in toluene at 25°C) and a 1,2-double bond content of 50%.

Mixture:

toluene 1700 g

polybutadiene 300 g

thioglycollic acid varied

temperature 75°C

AIBN 1.0 g

reaction time 7 hours

The reactions products were precipitated with methanol and dried *in vacuo* at 60°C until constant in weight.

Results

	Test No.	Thioglycollic acid g	$[\eta]$ dl/g ⁺	S observed %	S calculated %
5	1	26	1.25	2.7	2.7
	2	46	1.24	4.5	4.6
	3	67	1.24	6.1	6.2

+ in toluene at 25°C

EXAMPLE 3

10 A polybutadiene with a viscosity number $[\eta]$ of 1.03 dl/g (in toluene at 25°C) and a 1,2-double bond content of 40% was reacted with thioglycollic acid butyl ester in the same way as in Example 1. 10

Mixture:

	toluene	1600 g	
15	polybutadiene	430 g	15
	thioglycollic acid		
	butyl ester	varied	
	temperature	75°C	
	AIBN	1.6 g	
20	reaction time	7 hours	20

The reaction products were precipitated with methanol and dried *in vacuo* at 60°C until constant in weight.

Results

25	Test No.	Thioglycollic acid butyl ester g	$[\eta]$ dl/g toluene, 25°C	S observed %	S calculated %	25
	1	45	1.3	2.0	2.0	
	2	60	1.3	2.6	2.6	
	3	80	1.4	3.2	3.3	

30 Comparison tests

Polybutadienes with different 1,2-double bond contents were reacted with 2-mercaptoethanol under the reaction conditions described in Example 1. 30

Mixture:

	toluene	800 g	
5	polybutadiene with different 1,2-double bond contents	200 g	5
	mercaptoethanol	25 g	
	temperature	75°C	
	AIBN	0.8 g	
	reaction time	7 h	

10

The reaction products were isolated by precipitation with methanol.

10

Results

Test No.	Polybutadiene 1,2-double bond content %	$[\eta]$ dl/g toluene, 25°C	S observed %	S calculated %	
15	1 ^{a)}	crosslinked	0.5	4.6	15
	2	crosslinked	0.9	4.6	
	3	40 ^{c)}	1.8	4.5	4.6

a) Ni-type, ML-4'/100°C = 35, 1% 1,2-double bond content

b) Li-type, ML-4'/100°C = 35, 10% 1,2-double bond content

20 c) Li + donor-type, ML-4'/100°C = 35, 40% 1,2-double bond content 20

EXAMPLE 4.

Processing and vulcanisation

25 A polymer according to the invention with a Mooney viscosity ML-4' of 47 and a sulphur content of 4%, and, for comparison a polybutadiene having a 1,2-double bond content of 40% and a cis-1,4-polybutadiene, were tested in the following recipe (in parts by weight), which is typical of a mixture filled with highly active silica:

	Polymer	100	
	Highly active silica ¹⁾	90	
30	Polyether plasticiser ²⁾	25	30
	Naphthenic plasticiser ³⁾	25	
	Zinc stearate	3	
	Antiager 1 ⁴⁾	2	
	Antiager 2 ⁵⁾	1	
35	Sulphur	3.0	35
	Accelerator 1 ⁶⁾	1.8	
	Accelerator 2 ⁷⁾	0.2	

Footnotes to Example 4

- 1) = Volkasil S (Registered Trade Mark)
 2) = Desmophen 3900 (Registered Trade Mark)
 3) = Ingraplast S (Registered Trade Mark)
 4) = Vulkanox AFD (Registered Trade Mark)
 5) = Vulkanox DS (Registered Trade Mark)
 6) = Vulkacit DM (Registered Trade Mark)
 7) = Vulkacit D (Registered Trade Mark)

The mixtures were prepared in the usual way on laboratory mixing rolls and were subsequently vulcanised at 150°C. With an optimum heating time (30 min.), the following physical values were obtained with the polymer produced in accordance with the invention (mixture A):

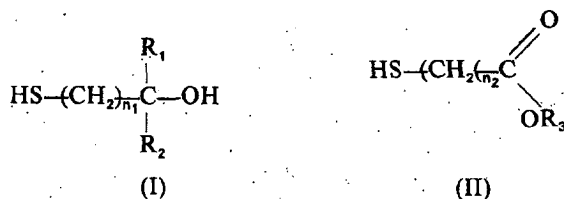
	A ¹⁾	B ²⁾	C ³⁾	
	14.5	5.0	7.7	
15 Tensile strength (MPa)				
Elongation at break (%)	500	150	200	15
Modulus at 300% elongation (MPa)	7.2	—	—	
Hardness at 23°C (Shore A)	71	65	78	
Tear strength according to Pohle (N)	200	100	100	
20 1) polymer according to the invention				
2) polybutadiene with a 40% 1,2-double-bond-content				20
3) cis-1,4-polybutadiene				

Mixture A could be processed without difficulty, whilst mixtures B and C could only be produced with considerable difficulty such as, for example, serious bagging, separation from the rolls and a greatly increased mixing time.

As shown by the tests, the vulcanisates produced in accordance with the invention are superior to the comparison polymers.

WHAT I CLAIM IS:—

1. A process for the production of a mercaptan-modified polybutadiene, which reacting in solution in an inert solvent a polybutadiene, having a 1,2-double bond content of from 30 to 60% and a viscosity $[\eta]$ of from 0.8 to 1.8 dl/g (as measured in toluene at 25°C), with a mercaptan corresponding to the general formula (I) or (II):



in which

- 35 R_1 , R_2 and R_3 , which may be the same or different, represent hydrogen or a straight-chain or branched alkyl or aryl radical,
 n_1 is a number from 1 to 4, and
 n_2 is a number from 1 to 5.

2. A process as claimed in claim 1, wherein the molar ratio of mercaptan to 1,2-double bonds in the polybutadiene is from 0.1 to 0.6.

3. A process as claimed in claim 1 or 2, wherein the reaction temperature is in the range of from 50 to 150°C.

4. A process as claimed in claim 1, substantially as hereinbefore described with reference to any of the Examples.

5. A mercaptan-modified polybutadiene produced by a process as claimed in any one of claims 1 to 4.

6. A rubber composition containing a mercaptan-modified polybutadiene as claimed in claim 5.

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